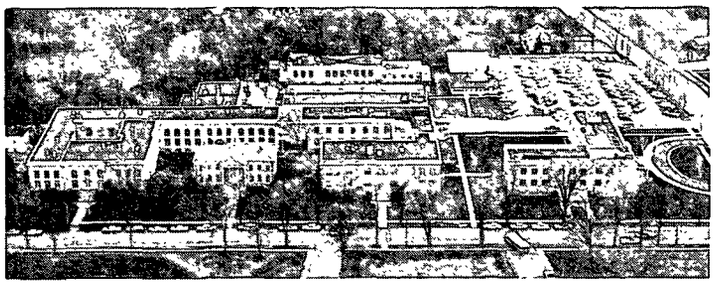

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FAST REACTIONS IN ALKALINE PULPING. I. A PRESSURIZED FLOW REACTOR FOR STUDYING FAST REACTIONS UNDER ALKALINE PULPING CONDITIONS

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FAST REACTIONS IN ALKALINE PULPING. I. A PRESSURIZED FLOW REACTOR FOR STUDY OF FAST REACTIONS UNDER ALKALINE PULPING CONDITIONS

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INTRODUCTION

Very short reaction times were obtained for liquid systems with a flow reactor, capable of operating at temperatures up to 170°C and pressures of 350 psi. Reactions were started by forcing two solutions containing reactants from syringes through a mixing tee into a reaction coil. The resulting reaction solution was pumped through the coil to a second tee where it was mixed with a quenching agent to stop the reaction. By use of syringes driven by hydraulic rams to give high flow rates through the mixers and the reaction zone, reaction times ranging from several minutes down to 10 milliseconds were obtained.

To obtain efficient mixing, the tees contained small "swirlers" which forced the two solutions through very small orifices into a mixing chamber. The hydraulic rams were necessary to overcome the resistance of these swirlers, i.e., work needed to accomplish mixing.

The syringes, coils and mixers were all fabricated of stainless steel to withstand pressure and reactions at elevated temperatures. The two reactant solutions were heated in heating coils and immersed in an oil bath before they were driven into the reaction coil, also immersed in the same bath. The quenching agent was maintained at room temperature so that it served to cool the reaction solution in addition to stopping the reaction by a chemical reaction. This quenching reaction must be very fast in comparison to the reaction being studied in the reaction coil.

The complete apparatus was maintained in a pressure chamber filled with nitrogen, for reactions above 100°C, to prevent the aqueous system from volatilizing.

The flow rate of the liquids was monitored electrically by measuring the movement of the syringes with a linear potentiometer, and recording this with a high speed oscillograph recorder.

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Fast reactions in alkaline pulping. I.

A pressurized flow reactor for studying fast reactions under alkaline pulping conditions

John W. Green, Keith W. Hardacker, and Bruce D. Andrews

Abstract

A flow reactor has been constructed, capable of operating under pressure to 300 psi and at temperatures up to 170 C. The reactions are started by rapid mixing of the reactants and terminated by rapid mixing with a quenching agent. Reaction times down to 10 milliseconds have been observed. The equipment, constructed of stainless steel, was designed to study fast alkaline pulping reaction.

INTRODUCTION

Flow reactors have been used for many years in the study of very fast biological reactions (1). Reaction times in the millisecond and microsecond range have been obtained. The original concept of a flow reactor depended on efficient mixing of the several reactants, so much work was done in this area (1,2). The reactions studied were confined to lower temperatures, and few reactions have been observed at higher temperatures.

The present paper deals with the construction and operation of a flow reactor capable of operating under pressures to 300 psi and at temperatures up to 170°C; the reactions are terminated by mixing with a quenching agent. Reaction times down to 10 milliseconds have been observed. Application has been made to some of the fast reactions occurring in alkaline pulping systems.

The operating principle of the flow reactor is shown in Fig. 1. Reactants A and B are forced simultaneously from syringes into heating coils, then mixed at M_1. The reaction solution is driven through reaction coil R. At mixer M_2, the reaction is terminated by addition of a quenching agent, C. The solution Q is then analyzed. The time of reaction, T_R, is directly proportional to the volume, V_c, of the reaction coil and inversely proportional to the flow rate of the liquid through the coil.

$$T_R = V_c/(\text{ml/sec}) = \text{seconds}$$

[Fig. 1 here]

The actual operation is composed of three phases. (a) The reaction syringes (20.8 ml each) are half-emptied into the heating coils (12 ml each). (b) After a given heating interval, the remainder of the solution in each syringe (10.4 ml) is pushed into the heating coils. This cold solution drives most of the heated solution (about 17 ml for both coils) through the reaction coil. (c) Just before the reaction solution enters the second mixer, quench reagent is pushed out of its syringe. The final volume of reaction solution obtained, before dilution with quench reagent, ranges from 12 to 17 ml, depending on the volume of the reaction coil (5 to 0.1 ml).

The solution remaining in the heating and reaction coils has an uncertain kinetic history, so the coils are rinsed out and dried before another run is made.

The volume of the quenching agent C is large (100 ml) compared to the volume of reaction solution leaving the reaction coil. It is essential that the latter volume be "bracketed" by quenching reagent, so that the reaction is terminated sharply for all the reaction solution passing through the second mixer. The bracketing is controlled automatically and is described below.

The flow rate of the reaction syringes ranges from 0.1 ml/sec to 14 ml/sec; the volume of the reaction coil, from 0.1 to 5 ml. Thus, a range of reaction times from 50 sec to 0.01 sec can be handled. All surfaces contacted by the solutions are of type 316 stainless steel or Teflon.

PRESSURE CHAMBER

Figure 2 shows the arrangement of the reaction (mix) and quenching syringes within the pressure chamber. These syringes and two hydraulic rams are mounted on a steel channel; the rams drive the syringes in either forward or reverse directions. The two mix syringes are mounted side by side and are driven by one ram. The heating and reaction coils are mounted outside the chamber, and form an external pressure loop; they are the only part of the reactor that is heated in the oil bath.

[Fig. 2 here]

The pressure chamber is sealed at each end with a blind flange, and is pressurized with nitrogen to prevent boiling of the aqueous solution. The flange at the right in the figure, containing connections to the hydraulic oil lines, is normally kept attached. The flange at the left is bolted on during operations, but is removed for insertion and removal of the quench bottle.

The syringes are connected by stainless steel tubing and pressure bulkhead fittings to the wall of the chamber (see Fig. 3). Valves outside the pressure chamber lead from these lines to the heating coils and to bottles of solutions used to fill the syringes (see Fig. 4).

[Fig. 3 and 4 here]

CONTROL OF SYRINGE MOVEMENTS

The movement of the stainless steel syringes inside the chamber is effected by hydraulic cylinders (rams) from a rack-mounted panel (see Fig. 5). Their positions are monitored on a Hathaway 460 oscillograph recorder via linear potentiometers.

[Fig. 5 here]

The Retract position of the mix ram control switch is used for filling the syringes. The Advance position will deliver 20.8 ml; the Advance to Set Point position will deliver 10.4 ml. The movements of the ram (and syringes) are precise; the volumes delivered will check within 0.05 ml. The output of the combined mix syringes (set by micrometer flow control of ram speed) ranges from 0.13 to 14.2 ml/sec.

The quench ram control switch includes an adjustable Delayed Advance position. The speed of the quench syringe delivery ranges from 1.0 to 27 ml/sec.

The automatic action of the set-point switches MS-1 and MS-2 are shown in Fig. 6. The two mix syringes are connected side by side to a common push bar, to which the hydraulic ram, the linear potentiometer, and the cam rod for the limit switches are also attached. The geometry is such that MS-1, originally riding in a high position for the full syringe, drops at the half-way position of the ram and stops the syringe movement (see end of $\underline{T_F}$ in Fig. 7). Later, during the second half-stroke ($\underline{T_K}$), MS-2 is turned on and initiates movement of the quenching syringe ($\underline{T_Q}$). The position of MS-2 is adjustable; it is set for the time when the reaction solution enters the second mixer. This switch will trigger only when the quench ram switch is set in the Delayed Advance position.

[Fig. 6 and 7 here]

The oscillograph recorder is used to measure the rate, volume, and timing of liquid flow from the several syringes; this can be done to 0.01 sec time. The syringe movements shown in Fig. 7 were taken from a recording of the signals from the two linear potentiometers.

The sequence of operations during an actual run is given later.

HEATING AND REACTION COILS AND MIXERS

The coils are made of 1/8-inch diameter, type 316 stainless steel tubing having a bore of 0.085 inch. The volumes of the coils were determined first by length (10.7 inches/ml) and then by connection to a reaction syringe and noting the difference in weight of liquid delivered by the latter. To prevent entrainment of air bubbles, the liquid is introduced at the bottom of the coils, both in the heating and reaction coils (see Fig. 4). The efficiency of the reactor depends on the introduction of definite volumes of liquid into the heating coils; this liquid should stop short of the mixer.

The efficiency of the reactor also depends on a maximum mixing effort with a minimum of dead volume for the mixing area. For this purpose, 8-jet mixers (8-mm diameter) of the Gibson type (2) are used. They are constructed of stainless steel and mounted in a housing fitted with Teflon washers. The small jets (0.02-inch diameter) offer considerable resistance to liquid flow; the pressure needed to overcome this reflects in the work done in the mixing process. The volume of two such jet mixers, with housings and connected by a 1-inch length of tubing 0.085-inch I.D., is 0.75 ml; the volume of each mixer is about 1/10 of this. Ideally, the mixing should occur in a region of near zero volume, but this is difficult to obtain.

Reaction coils of volumes below 1 ml were usually short lengths of tubing of I.D. of either 0.085 or 0.027 inch. With such small coils,

the amount of reaction occurring in the mixers becomes an appreciable factor.

MAKING A KINETIC RUN

About an hour is required to prepare the apparatus, make a run, and clean up for another run. The principal steps are given below. The positions of the ram control switches (see Fig. 5) are given in parentheses.

1. The mix and quench syringes are filled with solution. (Retract.)

2. The quench bottle is placed in the pressure chamber and the flange secured.

3. The empty coils and mixers are tested at 200 psig nitrogen for leaks. Any faulty Teflon washers are replaced.

4. The coils and mixers are attached. The valves are turned to connect the mix syringes to the heating coils and the quench syringe to the second mixer. (Delayed Advance.)

5. The heating coils are filled with the two reactants. (Advance to Set Point.)

6. The chamber is pressurized with nitrogen, and the coil bath raised to cover the coils and mixers.

7. After 6 minutes the recorder chart feed is turned on and the heated liquid forced through the reaction coil. (Advance, for Mix Ram.) The quenching syringe will be operated automatically.

8. The recorder is stopped, the bath lowered, and the coils cooled with water.

9. The pressure is relieved and the quench bottle removed. The flow rates are calculated from the recorder trace. The quench solution is immediately analyzed.

10. The coils and mixers are removed, rinsed with water and acetone, then dried.

There are also other steps to check the flow controls, correct positions of valves, etc. The several operations are rather complicated and we have found it best to have a detailed check list to follow for each run.

ACKNOWLEDGMENTS

Acknowledgment is made to the cooperators of Project 2942 at The Institute of Paper Chemistry, who made this work possible.

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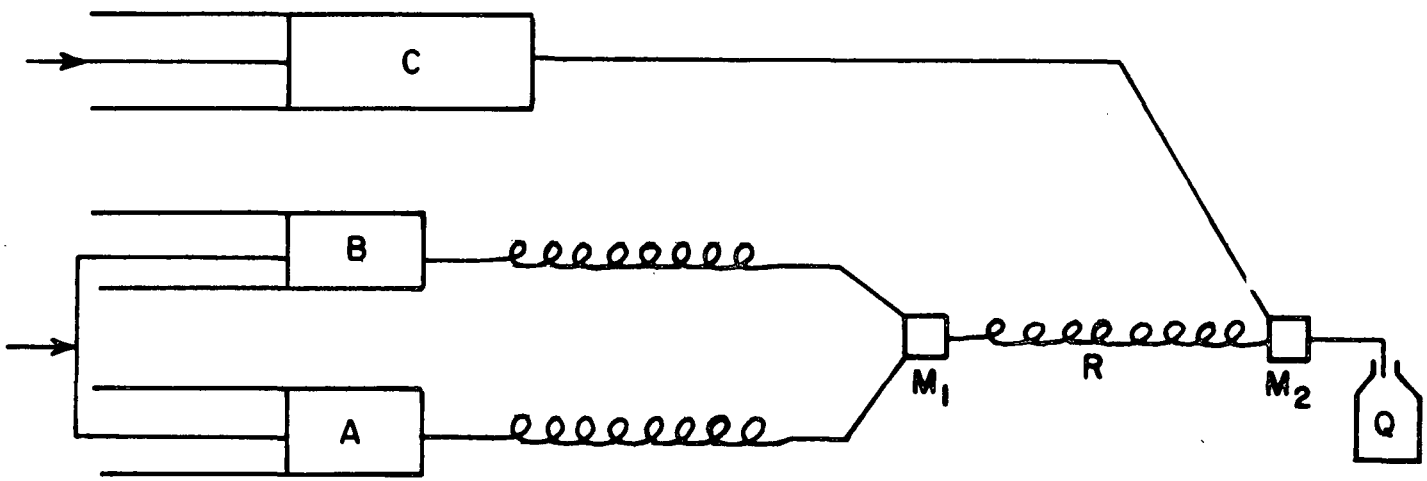

Fig. 1. Outline of a flow reactor. $\underline{M_1}$ and $\underline{M_2}$ are mixers, $\underline{R}$ is the reaction coil.

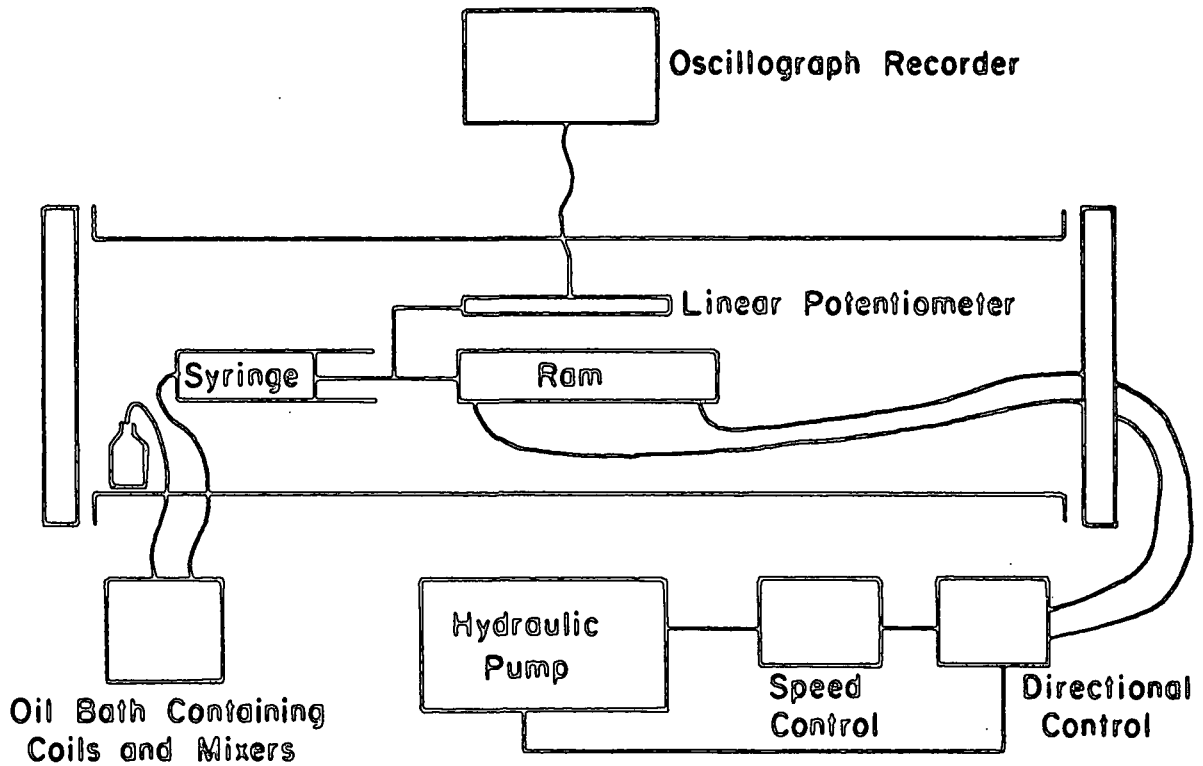

Fig. 2. Pressure chamber and arrangement of syringes and controls. Only one syringe is shown in the figure.

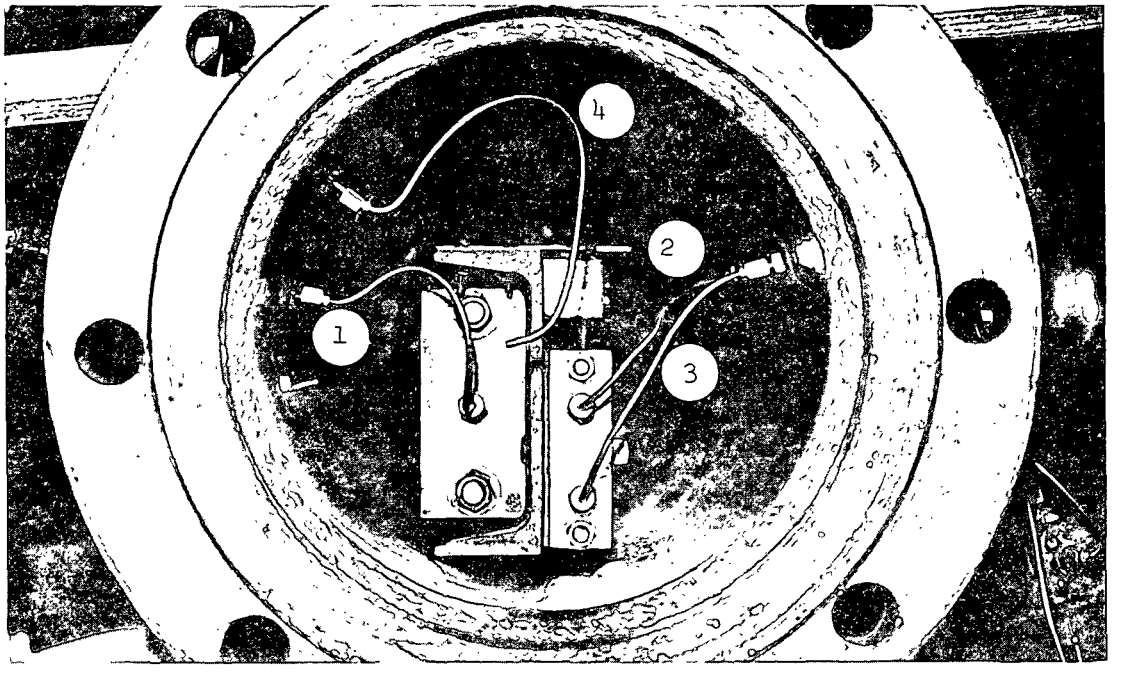

Fig. 3. End view of pressure chamber, showing syringe connections: (1) lead from quench syringe; (2,3) leads from mix syringes; (4) lead to quench bottle. The chamber is made from a 52-inch length of 8-inch steel pipe.

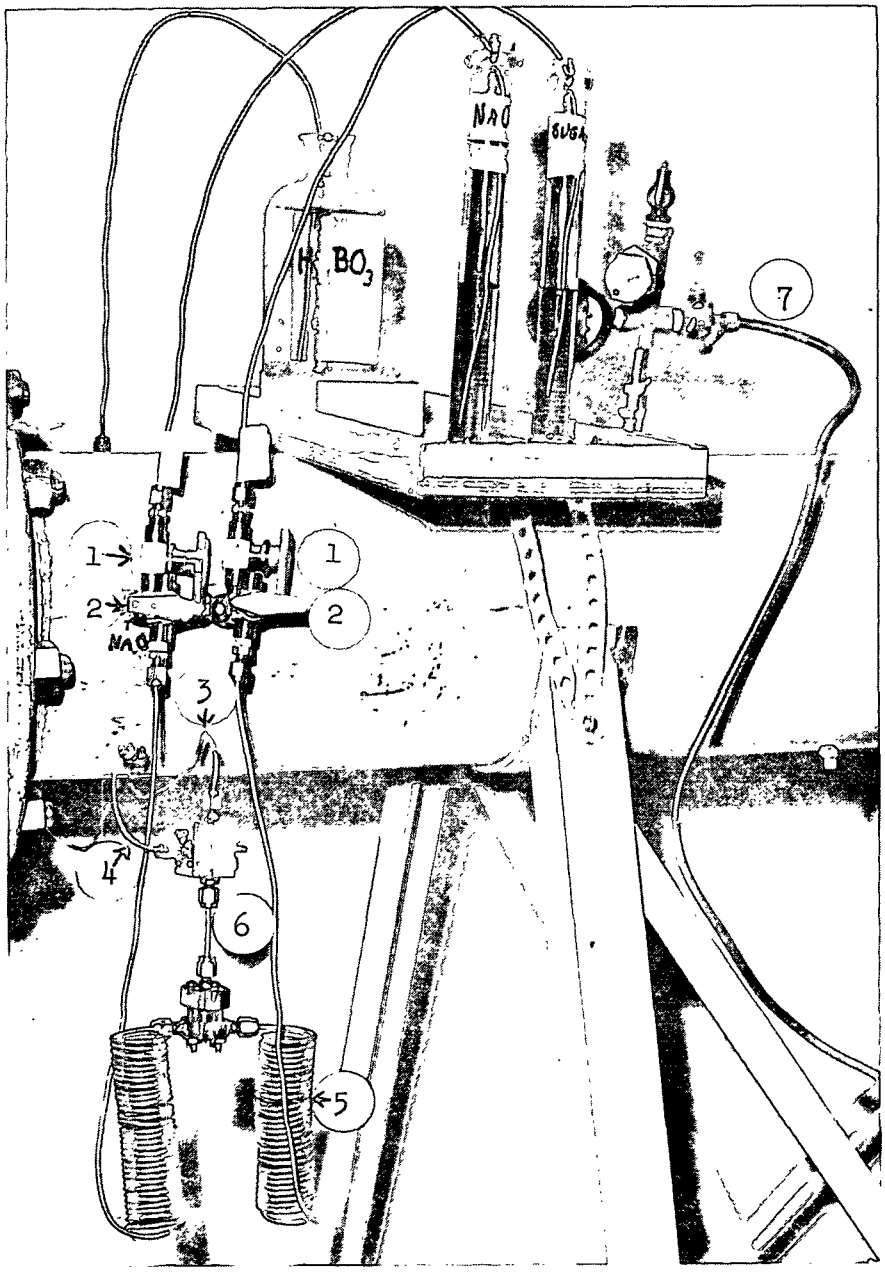

Fig. 4. Exterior arrangement of coils and mixers: (1) valves connected to mix syringes and solutions; (2) valves connected to syringes and heating coils; (3) lead from quench syringe to quench mixer; (4) lead from quench line to mixer; (5) heating coils; (6) reaction coil mounted between two mixers; coil has 0.02 ml volume; (7) nitrogen pressure line.

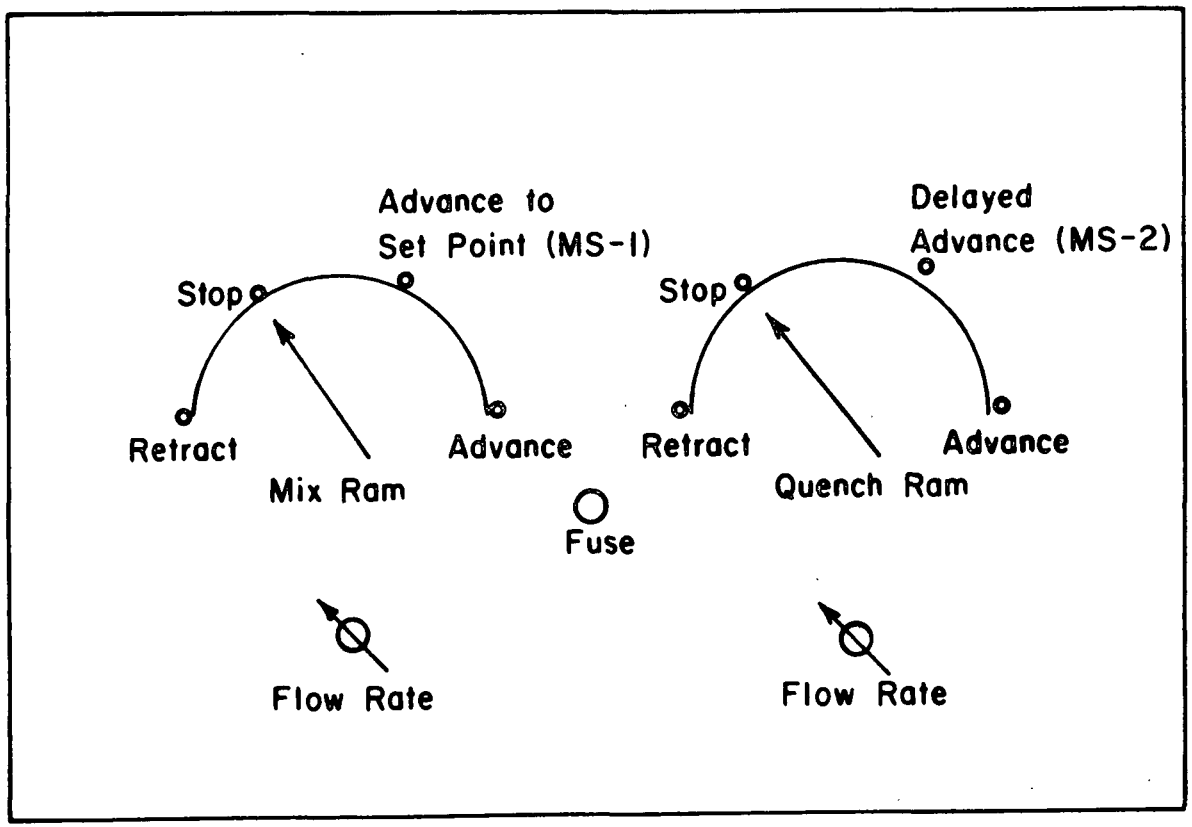

Fig. 5. Manual controls on syringe control panel.

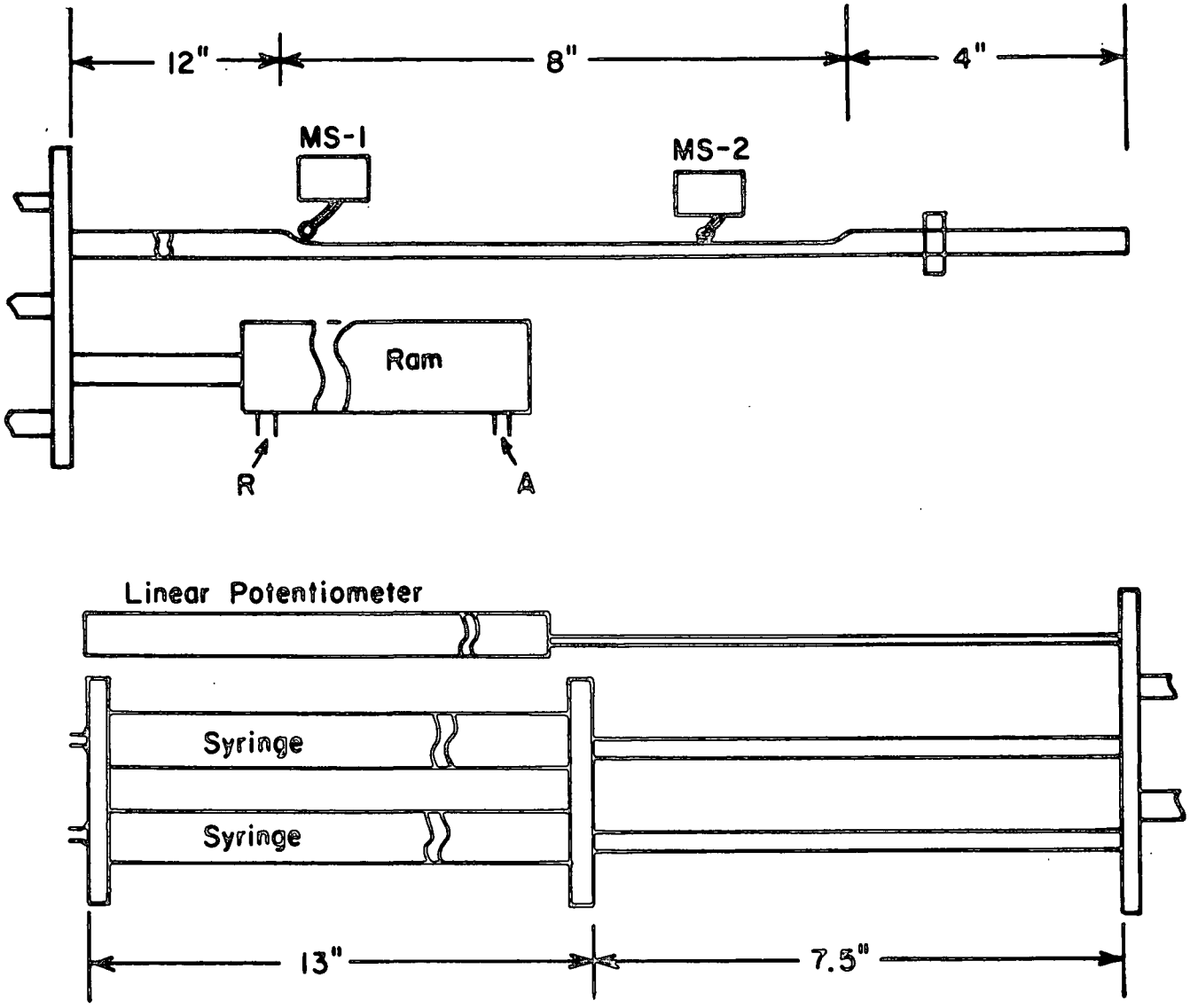

Fig. 6. Arrangement of reaction syringes, position potentiometer, hydraulic ram, and set-point switches.

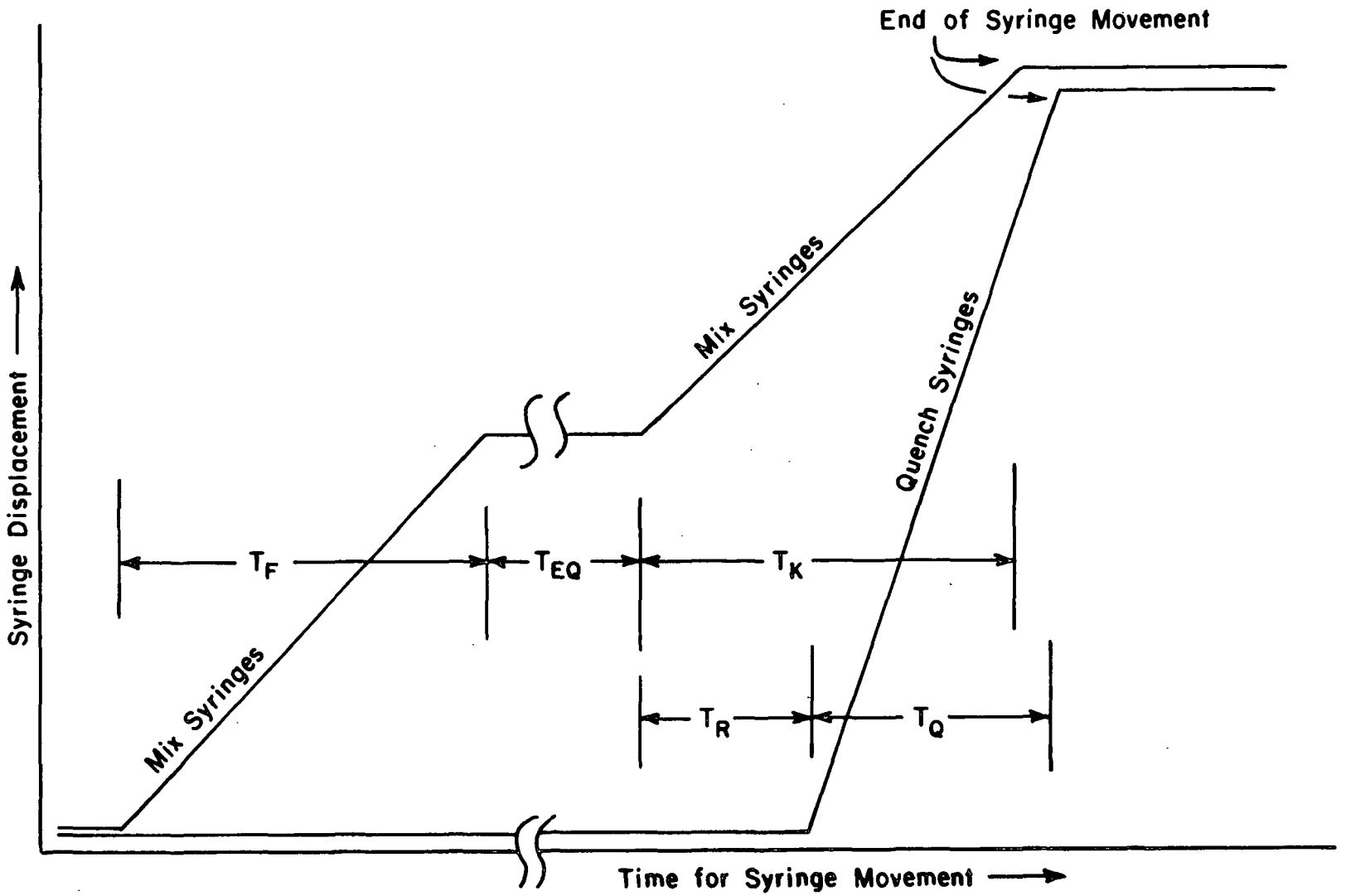

Fig. 7. Oscillograph recording of syringe movements. T_F = filling time; T_{EQ} = temperature equilibration time (2-6 min); T_K = time for 20.8 ml to move from two mix syringes; T_R = time for reaction solution to reach second mixer; T_Q = time for 100 ml of quench reagent to move from quench syringe.